

PRODUCTION OF HYDROGEN FROM HEMICELLULOSE-RICH FRACTIONS GENERATED THROUGH STEAM FRACTIONATION OF BIOMASS

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INTRODUCTION

Hydrogen is the most environmentally friendly fuel that can be efficiently used for power generation or transportation. At present, however, hydrogen is produced almost entirely from fossil fuels such as natural gas, naphtha, and inexpensive coal. In such a case, the same amount of CO₂ as that formed from combustion of those fuels is released during the hydrogen production stage. Renewable biomass is an attractive alternative to fossil feedstocks because of essentially zero net CO₂ impact. Unfortunately, hydrogen content in biomass is only 6-6.5% compared to almost 25% in natural gas. For this reason, on a cost basis, producing hydrogen by the biomass gasification/water-gas shift process cannot compete with the well-developed technology for steam reforming of natural gas. However, an integrated process, in which biomass is partly used to produce more valuable materials or chemicals with only residual fractions utilised for generation of hydrogen, can be an economically viable option.

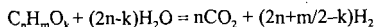
Biomass is comprised of three main constitutive bio-polymers: cellulose, hemicellulose, and lignin. When separated they can be further converted into commercial products of significantly higher value (especially cellulose) than that of the original biomass. Steam-aqueous fractionation is one of the technologies being developed for this application. The concept presented in this paper is an integration of steam-aqueous fractionation of biomass, with catalytic steam reforming of the lower-value hemicellulose-rich liquid by-product to produce hydrogen.

EXPERIMENTAL

Fractionation of poplar wood was performed in a continuous unit described elsewhere [1] employing steam treatment of poplar at a severity of $\text{Log } R_0=3.8$. Severity combines the effect of temperature and duration of the process using reaction ordinate defined as $\text{Log } R_0 = \text{Log } t + (T-100)/14.75$. This treatment led to solubilization, after washing, of 30% of the biomass into a hemicellulose-rich aqueous solution. The aqueous solution contained 32.1% of solutes having the elemental composition $\text{CH}_{1.36}\text{O}_{0.67}$. These solutes were mostly oligomeric pentosan and a small amount of dissolved lignin. The aqueous solution was then steam reformed using a bench-scale fluidized bed reactor shown in Figure 1. The two-inch-diameter Inconel reactor supplied with a porous metal distribution plate was placed inside a three-zone electric furnace. The reactor contained 150-200g of commercial nickel-based catalyst from United Catalysts ground to the particle size of 300-500 μ . The catalyst was fluidized using superheated steam, which is also a reactant in the reforming process. Steam was generated in a boiler and superheated to 750C before entering the reactor at a flow rate of 2-4 g/min. Liquids were fed at a rate of 4-5 g/min using a diaphragm pump. A specially designed injection nozzle supplied with a cooling jacket was used to spray liquids into the catalyst bed. The temperature in the injector was controlled by a coolant flow and maintained below the feed boiling point to prevent evaporation of volatiles and deposition of nonvolatile components. The product collection line included a cyclone that captured fine catalyst particles and any char generated in the reactor and two heat exchangers to condense excess steam. The condensate was collected in a vessel whose weight was continuously monitored. The outlet gas flow rate was measured by a mass flow meter and by a dry test meter. The gas composition was analyzed every 5 minutes by a MTI gas chromatograph. The analysis provided concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen in the outlet gas stream as a function of time of the test. The temperatures in the system as well as the flows were recorded and controlled by the G2/OPTO data acquisition and control system. The measurements allowed to determine total and elemental balances as well as to calculate the yield of hydrogen generated from the biomass-derived liquid feed.

RESULTS AND DISCUSSION

The overall steam reforming reaction of any oxygenated organic compound can be presented as follows:



Thus the maximum (stoichiometric) yield of hydrogen is $2+m/2n-k/n$ moles per mole of carbon in feed. Prior to the experiments of steam reforming complex biomass-derived liquids such as hemicellulose-rich solution obtained by biomass fractionation we performed tests using simpler model compounds (methanol, acetic acid, hydroxyacetaldehyde, syringol, and others). These tests were carried out using different commercial and research nickel-based catalysts designed for reforming natural gas and naphta. Results obtained employing a fixed-bed reactor configuration showed that within the temperature range 650-800°C and using commercial catalysts model compounds were converted to hydrogen with a yield greater than 85% of that possible for stoichiometric conversion [2-4]. However, the oligomeric compounds are more difficult to reform because of their tendency to decompose thermally in the reactor leading to char formation. The attempts of reforming hemicellulose-rich solutions in the fixed-bed reactor were not very successful [5]. After a short time (30 min), thermal decomposition led to the formation of carbonaceous deposits on and above the catalyst bed that resulted in an excessive pressure build-up in the system and made the deepest layers of the catalyst bed inaccessible to contact with the feed. Therefore, we decided to use a fluidized bed reactor for processing thermally unstable liquids because it exposes the whole amount of the catalyst to the contact with catalyst.

Steam reforming of the hemicellulose-rich liquid was carried out at the catalyst fluid bed temperature of 800°C with the feed rate of 4 g/min and steam flow of 2.4 g/min. The produced gas composition is shown in Figure 2. At the beginning of the run the hydrogen concentration was 65% but decreased to 60% after three hours on stream. This suggests that catalyst deactivated during the experiment. Hydrogen yield was 67.3% of that which could be obtained by stoichiometric conversion. Mass balances indicated that 73% of carbon from hemicellulose was converted to CO₂ and CO. The remaining 27% could thus form char entrained from the system and coke deposits on the catalyst surface, which would explain the loss of its activity. The activity of the catalyst used for reforming was easily restored by steam or carbon dioxide gasification of the deposits. The catalyst was reused in next experiments showing the same efficiency. The regeneration also resulted in producing additional amounts of hydrogen from the conversion of C (in coke) to CO + H₂ (in gas). At present, our efforts focus on finding optimum process conditions (temperature, steam to carbon ratio) to maximise hydrogen production and minimise coke formation.

CONCLUSIONS

Biomass can be a resource for hydrogen production providing that higher value fractions will be used for other applications. Hemicellulose-rich fraction from aqueous/steam fractionation of poplar wood was processed by catalytic steam reforming to generate hydrogen. So far tests have led to hydrogen yields of 67.3% of stoichiometric values. Fluidized bed is a better configuration than fixed-bed reactor for reforming biomass-derived liquid streams that tend to decompose thermally producing undesired carbonaceous residues. Catalysts used for steam reforming can be efficiently regenerated by steam or carbon dioxide gasification. The reforming process needs to be optimised to determine conditions that allow for maximum (near stoichiometric) yields of hydrogen and minimum coke formation.

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Gas Composition

The graph displays the percentage volume of three gases over a 200-minute period. The y-axis represents '% vol.' from 0 to 70, and the x-axis represents 'Time, min' from 0 to 200.

- H₂ (Hydrogen):** Represented by a solid line with solid circles. It starts at approximately 65% and remains relatively stable, fluctuating between 60% and 68% throughout the run.
- CO₂ (Carbon Dioxide):** Represented by a solid line with open triangles. It starts at approximately 30% and fluctuates between 25% and 35%.
- CO (Carbon Monoxide):** Represented by a solid line with solid squares. It starts at approximately 6% and fluctuates between 5% and 12%.

Time (min)	H ₂ (% vol.)	CO ₂ (% vol.)	CO (% vol.)
0	65	30	6
25	65	30	7
50	64	30	8
75	65	30	9
100	64	30	8
125	64	30	7
150	62	30	8
175	61	28	6
200	61	28	6